The Origins of the Benzotriazole Project, Its Versatility Illustrated by a New $^{-}{}^{-}C{=}CHCH^{+}OEt$ Synthon, and Novel Syntheses of α,β-Unsaturated Aldehydes and Ketones, Furans, Pyrroles and Allyl Ethers

Alan R. Katritzky,* Hong Wu, Linghong Xie, in collaboration with Stanislaw Rachwal, Bogumila Rachwal, Jinlong Jiang, Guifen Zhang, Hengyuan Lang

Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, USA

Fax +1(904)3929199; E-mail KATRITZK@PINE.CIRCA.UFL.EDU

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A historical introduction describes the discovery and progress of benzotriazole synthetic methodology. 3-(Benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)**, readily prepared from 3-(benzotriazol-1-yl)-3-ethoxyprop-1-ene **(4)** via zinc bromide promoted allylic rearrangement, undergoes lithiation and regiospecific single or double 3-alkylation to give products which undergo (i) hydrolysis to afford α,β-unsaturated aldehydes, (ii) silica gel promoted reverse allylic rearrangement of the benzotriazolyl group, followed by further alkylation and subsequent hydrolysis to furnish α,β-unsaturated ketones, (iii) intramolecular cyclizations to construct pyrroles and furans, and (iv) intermolecular nucleophilic substitution with Grignard reagents to provide allyl ethers.

Background to the Benzotriazole Project (by ARK)

My very first paper[1] was concerned with the preparation of *N*-substituted benzotriazoles for use in carbazole synthesis, but I little imagined at that time how dominant a role benzotriazole chemistry would play in my research forty years later. How did we uncover the great potential of benzotriazole? Far from being a chance discovery, it was the direct result of the systematic examination of structure–property relationships.

From the beginning of my career, I was interested in the systematization of heterocyclic chemistry. In the 1950s, the only available textbook on the subject was authored by Morton[2] who covered heterocyclic chemistry compound by compound in a very classical manner. I had long wanted to systematize and rationalize the apparently complex chemistry of the five- and six-membered heteroaromatic compounds, and in 1960, Jeanne Lagowski and I produced the textbook *Heterocyclic Chemistry*,[3] which concentrated on the underlying unity of the subject, and correlations between the reactions of the various classes of compound. A fundamental distinction was drawn between (i) the reactions of the heteroaromatic rings and the ways in which these are affected by the orientation and nature of substitutents, and (ii) the reactions of substituents and the ways in which these are affected by the nature of the heteroaromatic rings to which they are attached.

In 1960, it was already possible to systematize the reactions of substituents attached to *C*-atoms of heterocyclic rings, and a modified form of this systematic approach was adopted in both the first 1984 edition (co-editor-in-chief Charles Rees)[4] and the second edition (1996 forthcoming)[5] of *Comprehensive Heterocyclic Chemistry* (co-editors-in-chief Charles Rees and Eric Scriven), as well as in the overview summary volume *Handbook of Heterocyclic Chemistry*.[6] However, substitutions can also be attached to heteroatoms in heterocyclic rings, most importantly to nitrogen atoms. When I started research in 1950, it was clear that, in contrast to *C*-linked substituents, the systematic chemistry of substituents connected to *N*-atoms of heteroaromatics was almost completely unstudied. A large part of my research has been devoted to exploring the chemistry of heteroaromatic *N*-substituents. Thus an early interest was generated in *N*-oxide chemistry[7,8] and this, with extensions into *N*-imides,[9] occupied much of our efforts in the 50s and 60s. Among substituents linked to a heterocyclic nitrogen by a carbon atom, we can distinguish between those attached to a positively-charged pyridinium-like nitrogen and those attached to a neutral pyrrole-like nitrogen. During the 70s and 80s, a significant part of my research effort was directed to a study of the reactions of *N*-substituents of pyridinium salts.[10] Attention was also given to the substituents attached to a *N*-atom of neutral azole rings, especially to the *N*-lithiation of *N*-substituents,[11] to rearrangements of *N*-substituted azoles,[12,13] and to *N*-amino compounds.[9] Early in 1984, as part of this systematic exploration of the reactivity of azoles, I asked Stan Rachwal, then a Postdoctoral Fellow with me, and Bogumila Rachwal, at the time a visiting scholar, to look in detail at *N*-substituted benzotriazoles. In was soon clear that we were on to something important, and in the 15 months before they returned to Poland in April 1985, they had already completed most of the experimental work for the first batch of 6 papers, which were published together in *J. Chem. Soc., Perkin Trans. 1* in 1987.[14] Since then, together with a group of most able collaborators, we have published some 200 papers on the chemistry of *N*-substituted benzotriazoles and the well shows no sign of running dry.

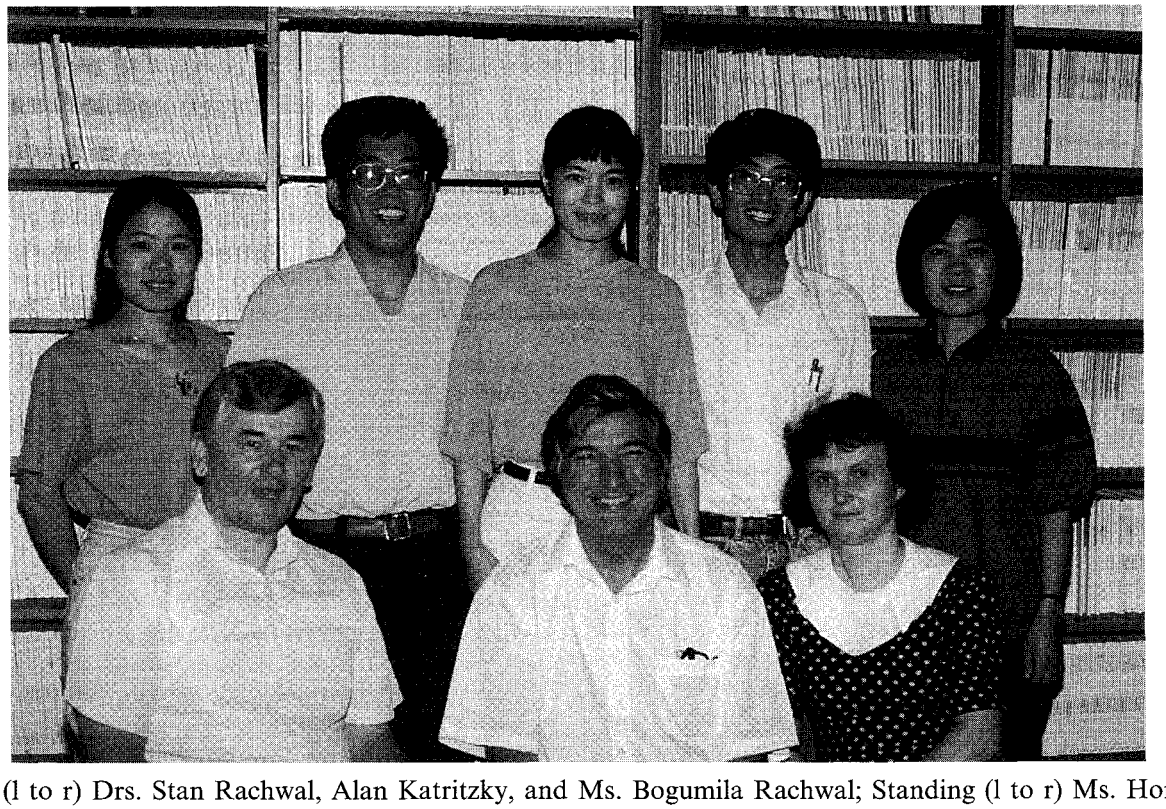
Why is benzotriazole so effective as a synthetic auxiliary? Its versatility depends on the interplay of five characteristic types of reactivity, of which the three most important were apparent from the beginning. Benzotriazole is cheap and readily recycled; add to this the ease in preparing and manipulating these compounds and their stability, and their importance is not surprising.

A. Behavior as a Leaving Group: A benzotriazol-1-(or -2-)yl is a leaving group of the same character as cyano, RO–, RS–, RS(O)– and $RS(O_2)$–. All of these are good leaving groups only when activated in one of two alternative ways: (i) by an electron donor substituent attached

to the same sp^3-hybridized carbon atom (or vinylogously to that *C*-atom); (ii) by an electron acceptor as when the group is attached to an sp^2- (or *sp*-) hybridized carbon atom which also carries an (directly or vinylogously) attached double bond to oxygen or nitrogen. Significantly, none of these groups behaves as a leaving group (iii) when attached to an unactivated sp^3- (or sp^2-) hybridized carbon. The halogens and tosylate behave as leaving groups in all of the situations (i), (ii), and (iii), but especially in situation (i) such compounds are often so reactive as to be difficult to isolate.

It turns out to be easy to prepare compounds of the type Bt–CH(R)–X and these react with nucleophiles to give Nu–CH(R)–X. Reactions of this type belong to the general class of "α-heteroalkylations". Where X = NR_2, it is an amino–alkylation. When X = OR, the reaction is an alkoxyalkylation, and when X = SR a thioalkylation. Reactions of this type have been carried out with a wide variety of nucleophiles: Nu = $H(BH_4^-)$, R (Grignards, alkylzincs), CN, aryl (reactive aromatics), heteroaryl (pyrroles, indoles, thiophenes, furans), NR_2 (amines, amides), etc.

Biographical Sketches



Seated (l to r) Drs. Stan Rachwal, Alan Katritzky, and Ms. Bogumila Rachwal; Standing (l to r) Ms. Hong Wu, Drs. Jinlong Jiang, Linghong Xie, Hengyuan Lang, and Ms. Guifen Zhang.

Biographical Sketches

Alan Katritzky (since 1980) Kenan Professor and Director of the Center for Heterocyclic Compounds at the University of Florida, was educated at Oxford, served on the Faculty at Cambridge, and from 1963–1980 was Foundation Professor of Chemistry (including 11 years as Dean) at the University of East Anglia, which recently awarded him his fourth honorary doctorate. His research through 1993 is summarized in *Heterocycles* **1994**, *37*, 3–130 (which was dedicated to him), and a light-hearted account of his life has appeared in *J. Heterocycl. Chem.* **1994**, *31*, 569–602.

Stan Rachwal is with Pharmos Inc., Alachua, Florida. Educated at Jagiellonian University, Poland and later on the faculty there, he pioneered benzotriazole chemistry in the Katritzky group in 1984–1985 and 1988–1992.

Bogumila Rachwal (M.S., Jagiellonian Univ.) remains with the group.

Linghong Xie gained her Ph.D. with Dr. Katritzky and is now a Group Leader at the Center for Heterocyclic Compounds.

Jinlong Jiang gained his Ph.D. with Dr. Katritzky, was a Group Leader, and has recently joined Merck as a research chemist.

Hengyuan Lang (Ph.D., Beijing Inst. of Technology) is also a Group Leader.

Hong Wu (M.S., Zhejiang Univ.) and **Guifen Zhang** (B.S., Hangzhou Univ.) from the People's Republic of China are Visiting Researchers at the Center for Heterocyclic Compounds.

B. Behavior as an Electron Donor: In benzotriazoles, all the nitrogen atoms including that to which a substituent is attached, are sp^2-hybridized. Thus the lone pair in a *p*-orbital, perpendicular to the ring plane, forms part of the aromatic electronic system; however, it is also available for conjugation with a carbocation center on the α-carbon atom of the substituent. Thus, in suitable systems of type Bt–CH(R)–X, the X group can behave as the leaving group and react with a nucleophile. Reaction with a nucleophile can give Bt–CH(R)–Nu. Reactions of this type, known as "α-benzotriazolylalkylations", are possible with a wide range of nucleophiles, and provide an important entry into starting materials for α-heteroalkylations as described above.

Recent reviews have dealt with benzotriazolylalkylations and benzotriazole-mediated heteroalkylation[15] and with benzotriazole-mediated arylalkylation and heteroarylalkylation.[16]

C. Behavior of an Activator of Proton Loss: Because of the considerable aromaticity of the benzotriazole ring, and the presence of two electron-attracting pyridine-like nitrogen atoms, a hydrogen atom on a carbon directly attached to the 1- or 2-position of benzotriazole can be detached as a proton in a reaction of type Bt–CHXY → Bt–C$^-$XY. The carbanion can be captured by a wide range of electrophiles which enlarges greatly the scope of the "α-heteroalkylation" and "α-benzotriazolylalkylation" reactions mentioned above. Significantly, the benzotriazole group diverts the incoming electrophile regiospecifically into the adjacent α-position in allylic systems. It is some recent work in this area that the present account will address.

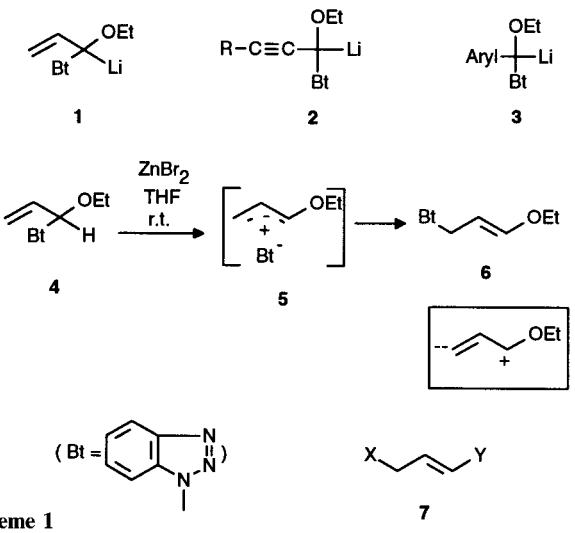
D. Behavior as a Radical Stabilizer: Recently, it has become apparent that a radical center is stabilized when attached at the 2-position of benzotriazole:[17] this feature is still under investigation.

E. Behavior Involving Ring Scission: Although in nearly all synthetic applications of benzotriazole the ring remains intact, there are exceptions.[18] Recently, synthetically useful applications of such reactions have been found.[19,20]

Benzotriazole-Stabilized Carbanions

Our work in this area through 1993 has been summarized.[21] Recently we have particularly exploited the ease of the formation by direct lithiation of derivatives of types **1**,[22] **2**[23] and **3**,[24] the regiospecific reaction of such compounds with electrophiles, and the facile hydrolysis of the products to form carbonyl compounds. We have now found that **4** undergoes smooth zinc bromide promoted rearrangement into **6** (Scheme 1). This paper introduces **6** as a valuable three-carbon homologating agent which provides a [$^-$C=CHCH$^+$OEt] synthon, with uses that complement our recent work on the [$^-$CH=CHCH$^+$NR$_2$) synthon.[25]

Three-carbon homologating agents have been extensively investigated.[26] 1,3-Diheteroatom-substituted propenes **7** have shown attractive features for carbon–carbon bond formation via lithiation and incorporation of electrophiles into the 1- or 3-position, followed by the further



Scheme 1

elaboration of the labile vinylic moiety.[25,27–30] Their synthetic utility and versatility depends greatly on their availability and on the regioselectivity of the reactions between their ambident allylic anions with electrophiles. We now report that readily available 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** undergoes lithiation and regiospecific single or double 3-alkylation. The alkylation products of **6** provide novel routes to (i) α,β-unsaturated aldehydes, (ii) α,β-unsaturated ketones, (iii) furans and pyrroles and (iv) allyl ethers.

Allylic 1,3-Rearrangement of the Benzotriazolyl Group: 3-(Benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)**, *Its Lithiation and Treatment with Electrophiles:* Treating compound **4** with zinc bromide in dry tetrahydrofuran at 20 °C gives 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** (95 %, 99 % purity), exclusively as the *E*-isomer. The disappearance of a 1H multiplet at ca. $\delta = 6.5$ (BtCH of **4**), and the existence of a 2H doublet at ca. $\delta = 5.2$ (BtCH$_2$ of **6**) in the ^{1}H NMR spectrum, indicated complete transformation. Structure **6** was fully characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. As shown in Scheme 1, this rearrangement probably involves intermediate **5**, allowing the exclusive production of the thermodynamically more stable derivative **6**. Zinc bromide induced facile cleavage of the benzotriazolyl anion is consistent with our previous observations.[31,32] The literature describes 1,3-rearrangements of allylic sulfonyl[33,34] phenylthio[35] and phenylsulfinyl groups,[34] but allylic rearrangement of the benzotriazolyl group was previously unknown.

Treatment of 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** with butyllithium at −78 °C, under argon in tetrahydrofuran, furnished a deep green solution of the lithio derivative of **6**. Reaction of this ambident allylic anion with an electrophile resulted in exclusive formation of the 3-alkylation product **8**. As an example, compound **8a** was prepared in 95 % yield when methyl iodide was used as the electrophile, and its structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. However, in general products **8** were advantageously subjected to further reactions carried out in one pot as illustrated by Schemes 2, 3 and 4.

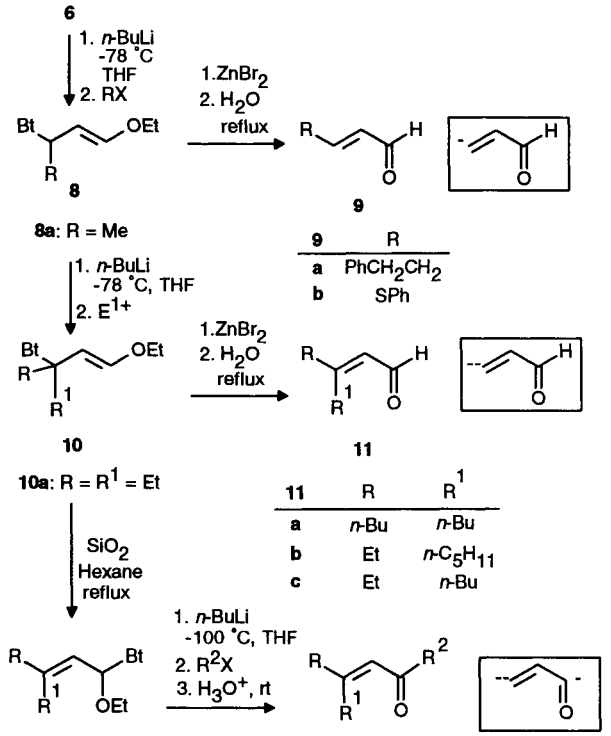
Introduction of two electrophiles into **6** can also be easily accomplished by successive regiospecific reaction of the allylic moiety with electrophiles. As exemplified by the synthesis of compound **10a**, the lithio derivative of **6** was reacted with ethyl iodide at −78 °C in tetrahydrofuran. After 5 hours, the solution was treated with butyllithium, followed by the addition of another equivalent of ethyl iodide to afford the diethylated product **10a** in 94% yield. That the alkylations occurred in a regiospecific manner at the 3-position was clearly indicated by the two doublets for the two vinylic protons in the ^{1}H NMR spectrum of **10a**. Of special interest is that the second alkylation took place regiospecifically at the more hindered carbon. The 1-methoxy group evidently enhances the reactivity of the 3-position of the lithio derivative of **8**, giving rise to this unique regioselectivity, cf.[36] Derivative **10a** was characterized by its ^{1}H and ^{13}C NMR spectra and elemental analysis. Other derivatives **10** were used without isolation for further transformation as discussed below.

In dialkylated compounds **10** the position α to the benzotriazolyl group is highly congested, and thus the benzotriazolyl group in **10** should be able to migrate back to its original position α to the ethoxy group to give thermodynamically more stable alkenes. Indeed, compound **10a** underwent this allylic rearrangement with ease in refluxing hexane in the presence of dry silica gel, to afford compound **12a** in almost quantitative yield. The structure of **12a** was confirmed by its ^{1}H and ^{13}C NMR spectra and high resolution mass spectrum. In this case no Lewis acid was required; two alkyl groups facilitate the rearrangement by stabilizing the transient cation. Again, derivatives **12** are advantageously used directly without isolation, see below.

Preparation of α,β-Unsaturated Aldehydes: After quenching the lithio derivative of **6** with 2-phenylethyl iodide and phenyl disulfide respectively, zinc bromide and water were successively added to the reaction mixture. β-Substituted (*E*)-α,β-unsaturated aldehydes **9a** and **9b** were thus produced in 82% and 45% overall yields via the concurrent hydrolysis of the vinyl ether moiety, and elimination of the benzotriazolyl group of intermediates **8**. In this transformation, **6** functions as a synthetic equivalent of the 2-formylethenyl carbanion ($^-$CH=CHCHO).

Similar to aldehydes **9**, β,β-disubstituted α,β-unsaturated aldehydes **11** were also synthesized in one pot from **6** via nonisolated intermediates **8** and **10** (Scheme 2). Successive alkylations utilized butyl iodide twice for **11a**, ethyl iodide and pentyl iodide for **11b** and ethyl iodide and butyl iodide for **11c**. The reaction mixtures were each subjected to hydrolysis with zinc bromide and water to furnish compounds **11a–c** in 72% to 78% overall yields. In the cases of **11b** and **11c**, mixtures of *cis*- and *trans*-isomers were obtained (Table 1). In this reaction sequence, compound **6** was shown to serve effectively as an α-fomylethenyl dianion ($^{--}$C=CHCHO) equivalent.

Preparation of α,β-Unsaturated Ketones: The ease of the transformation **10** → **12** enables the efficient construction of highly substituted α,β-unsaturated ketones. As

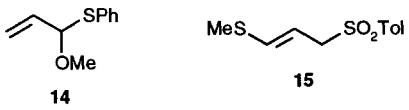


Scheme 2

shown in Scheme 2, compounds **13a** and **13b** were readily prepared in one-pot sequences from **6** in 66% and 50% overall yields via double butylation, followed by silica gel promoted rearrangement, a subsequent third alkylation [dimethyl(octyl)silyl iodide for **13a** and pentyl iodide for **13b**], and hydrolysis. Importantly, the third electrophile was again introduced regiospecifically into the position α to the benzotriazolyl group, which is consistent with our previous results.[22] In this synthetic transformation, 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** exhibits a trinucleophilic character and acts as a trianion equivalent of the type [O=C$^-$CH=C^{--}].

Since the pioneering work of Corey,[37] synthetic equivalents of β-acylvinyl anions have been sought actively. However, most such previously reported reagents function as β-formylvinyl monoanion ($^-$CH=CHCHO) equivalents: only one electrophile can be incorporated into the β-position.[30,37–40] β-Formylvinyl dianion ($^{--}$C=CHCHO) equivalents are less common, and only a single trianion (O=C$^-$CH=C^{--}) equivalent has been realized. The most important known reagents of these types are α-methoxyallyl sulfide **14** and 3-methylthioprop-2-enyl *p*-tolyl sulfone **(15)**. Compound **14** is a dianion ($^{--}$C=CHCHO) synthon equivalent leading to α,β-unsaturated aldehydes,[35] while compound **15** is effective both as a dianion ($^{--}$C=CHCHO)[41] and a trianion (O=C$^-$CH=C^{--}) equivalent[42] for the synthesis of α,β-unsaturated aldehydes and ketones. However, synthetic applications of **14** and **15** are limited by their re-

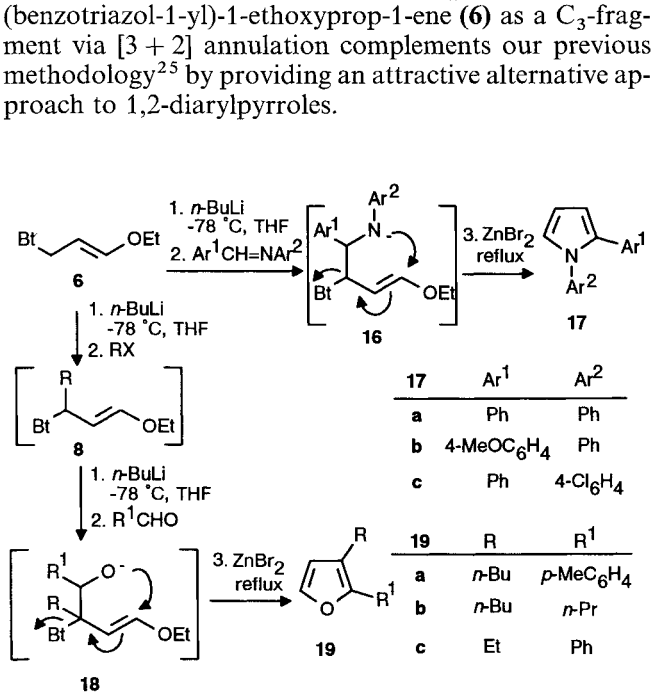
latively low availability.[41,43] Our present method using 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** combines the advantages of a readily available starting material, high versatility, mild conditions and simple one-pot procedures.



14 **15**

Preparations of 1,2-Diarylpyrroles and 2,3-Disubstituted Furans: Treatment of **6** with butyllithium at −78 °C, followed by the addition of diarylimines and heating in the presence of zinc bromide yielded 1,2-diarylpyrroles **17a–c** in 55–63% yields (Scheme 3), presumably via intermediates **16**, which underwent the equivalent of intramolecular S_N2' nucleophilic substitution and elimination of ethanol.

Until our previous publication,[25] many simple 1,2-diarylpyrroles of potential importance in medicine and technology[44,45] were still unknown. The present use of 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** as a C_3-fragment via [3 + 2] annulation complements our previous methodology[25] by providing an attractive alternative approach to 1,2-diarylpyrroles.



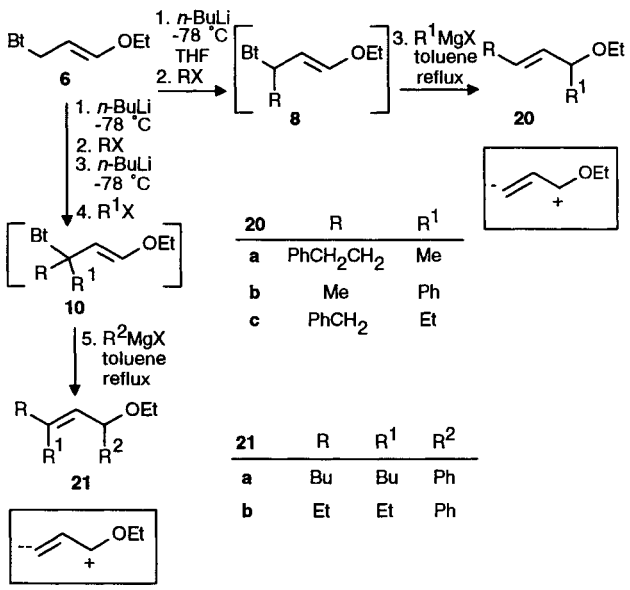
17	Ar^1	Ar^2
a	Ph	Ph
b	4-$MeOC_6H_4$	Ph
c	Ph	4-ClC_6H_4

19	R	R^1
a	*n*-Bu	*p*-MeC_6H_4
b	*n*-Bu	*n*-Pr
c	Et	Ph

Scheme 3

Following a similar protocol, substituted furans are accessible from reactions with aldehydes (Scheme 3). To introduce substituents into the 3-position of furan, the lithio derivative of **6** was first reacted with an alkyl halide (butyl iodide for **19a** and **19b** and ethyl iodide for **19c**). The resulting intermediates **8**, without separation, were treated with butyllithium followed by aldehydes to yield adducts **18**, which upon exposure to zinc bromide cyclized to 1,2-disubstituted furans **19a–c** in 46% to 52% total yields. Furans are important natural products, pharmaceuticals and synthetic intermediates. Numerous synthetic routes to furans are known.[32,46,47] Approaches to 2,3-disubstituted furans involving 1,3-diheteroatom-substituted propenes as three-carbon fragments include the [3 + 2] annulations of 3-methoxy-1-phenylthiopropene[35] and 1-benzyloxy-3-(*p*-tolylsulfonyl)alkenes[48] with aldehydes. However, 3-(benzotriazol-1-yl)-1-ethoxyprop-1-ene **(6)** is more readily accessible than these reagents and our procedures are simple.

Preparation of Allyl Ethers: We have shown that the benzotriazolyl groups in **16** and **18** are easily displaced by intramolecular nucleophiles to provide pyrroles and furans (Scheme 3). By analogy with these transformations, the alkylation products of **6** underwent intermolecular nucleophilic substitution with Grignard reagents to furnish various allyl ethers (Scheme 4). Accordingly, alkylation products **8** (from stepwise treatments of **6** with butyllithium and an alkyl halide) underwent S_N2' nucleophilic substitution, in situ, with Grignard reagents in refluxing toluene to afford allyl ethers **20a–c** in 60% to 71% total yields. Similarly, highly substituted allyl ethers **21a, b** were synthesized in 76% and 78% overall yields from **6** by treatment of the dialkylated intermediates of **6** with Grignard reagents in refluxing tetrahydrofuran. Thus, compound **6** provides [$^-$CH=CHCH$^+$OEt] and [$^{--}$C=CHCH$^+$OEt] fragments for the synthesis of allyl ethers.



20	R	R^1
a	$PhCH_2CH_2$	Me
b	Me	Ph
c	$PhCH_2$	Et

21	R	R^1	R^2
a	Bu	Bu	Ph
b	Et	Et	Ph

Scheme 4

The well established methodology via the reaction of allyl halides and alkoxides[49] is limited to structurally simple allyl ethers due to the low availability of the corresponding bromides. Our present method is related to previous preparations of allyl ethers by the addition of suitable nucleophiles to α-ethylenic acetals.[50] However, it is the first example to enable the construction of specific allyl ethers in a one-pot process via successive attachments of two or three different species to the three-carbon unit.

Conclusions

Readily available 3-(benzotriazol-yl)-1-ethoxyprop-1-ene **(6)** has been shown to be a useful and versatile three-

Table 1. Preparation of α,β-Unsaturated Aldehydes **9a,b**, **11a-c** and Ketones **13a,b**, Pyrroles **17a-c**, Furans **19a-c**, Allyl Ethers **20a-c**, **21a,b**

Compound	Yield [a] (%)	Molecular Formula	CHN Analyses / HRMS					
			Calc.			Found		
			C	H	N	C	H	N
9a	82 [b]	$C_{17}H_{16}N_4O_4$	60.00	4.74	16.46	59.81	4.81	16.39
9b	40	C_9H_8OS	65.82	4.95		65.73	4.91	
11a	78	$C_{11}H_{20}O$		168.1514			168.1519	
11b	76 [c]	$C_{10}H_{18}O$		154.1358			154.1408	
11c	72 [d]	$C_9H_{16}O$		140.1201			140.1275	
13a	66	$C_{21}H_{42}OSi$	74.48	12.50		74.16	12.63	
13b	50	$C_{16}H_{30}O$		239.2297			239.2311	
17a	55	$C_{16}H_{13}N$	87.64	5.98	6.39	87.54	6.13	6.31
17b	57	$C_{17}H_{15}NO$		249.1154			249.1156	
17c	63	$C_{16}H_{12}NCl$	75.74	4.77	5.52	75.37	4.68	5.43
19a	46	$C_{15}H_{18}O$	84.07	8.47		83.90	8.57	
19b	49	$C_{11}H_{18}O$	79.46	10.91		79.16	10.95	
19c	52	$C_{12}H_{12}O$	83.69	7.02		83.39	7.18	
20a	68	$C_{14}H_{20}O$	82.30	9.87		82.18	9.66	
20b	71	$C_{12}H_{16}O$	81.77	9.15		81.45	8.71	
20c	60	$C_{14}H_{20}O$	82.30	9.87		82.01	9.56	
21a	76	$C_{19}H_{30}O$	83.14	11.03		82.99	10.87	
21b	78	$C_{15}H_{22}O$	82.52	10.16		82.34	10.35	

[a] Overall yield from **6**.

[b] Isolated as 2,4-dinitrophenylhydrazine derivative.

[c] Mixture of *cis*- and *trans*- isomers (~ 1 : 1).

[d] Mixture of *cis*- and *trans*- isomers (*cis* : *trans* = 7 :13).

carbon homologating reagent. It functions as a synthetic equivalent of 2-formylethenyl monoanion ($^-CH=CHCHO$), dianion ($^{--}C=CHCHO$) and trianion ($O=C^-CH=C^{--}$) as demonstrated by the preparation of α,β-unsaturated carbonyl compounds, pyrroles and furans. It can also provide both [$^-CH=CHCH^+OEt$] and [$^{--}C=CHCH^+OEt$] fragments for the synthesis of allyl ethers.

NMR spectra were recorded in $CDCl_3$ on a 300 MHZ spectrometer. THF was distilled under N_2 immediately before use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out in atmospheres of argon. Column chromatography was conducted with silica gel grade 230–400 mesh. 3-(Benzotriazol-1-yl)-3-ethoxyprop-1-ene (**4**) was prepared according to our previous procedure.[22]

3-(Benzotriazol-1-yl)-1-ethoxyprop-1-ene (6):

A mixture of 3-(benzotriazol-1-yl)-3-ethoxyprop-1-ene (**4**; 20.3 g, 100 mmol) and $ZnBr_2$ (22.5 g, 100 mmol) in dry THF (300 mL) was stirred at r.t. under argon overnight. Et_2O (300 mL) was added and the mixture was washed with NaOH (5%, 2 × 100 mL), then H_2O (150 mL). The organic layer was dried ($MgSO_4$) and the solvent removed to give pure **6** as an oil; yield: 19.3 g (95%).

$C_{11}H_{13}N_3O$ (203.2): calc. C 65.01, H 6.45, N 20.67; found C 65.36, H 6.62, N 20.85.

^1H NMR: δ = 8.07 (dd, 1 H, J = 8.3, 1.0 Hz), 7.58 (dd, 1 H, J = 7.3,

0.9 Hz), 7.51–7.46 (m, 1 H), 7.40–7.35 (m, 1 H), 6.78 (d, 1 H, J = 12.6 Hz), 5.21 (d, 2 H, J = 7.5 Hz), 5.10–5.04 (m, 1 H), 3.77 (q, 2 H, J = 7.0 Hz), 1.29 (t, 3 H, J = 7.0 Hz).

^{13}C NMR: δ = 151.1, 146.3, 132.6, 127.0, 123.7, 119.9, 109.8, 97.0, 65.0, 47.5, 14.5.

3-(Benzotriazol-1-yl)-1-ethoxybut-1-ene (8a):
To a solution of **6** (10 mmol) in THF (40 mL) was added BuLi (2 M, 5.25 mL, 10.5 mmol) at − 78 °C under argon. After 45 min, MeI (1.42 g, 10 mmol) was added. The mixture was stirred for 4 h at − 78 °C and allowed to warm to r.t. overnight. The reaction was quenched with H_2O (100 mL) and the mixture extracted with Et_2O (3 × 70 mL). The organic layer was dried ($MgSO_4$) and the solvent removed to give reasonably pure **8a** as a colorless oil; yield: 2.06 g (95%). In order to get analytically pure compound, the crude was subjected to column chromatography (hexanes: EtOAc = 4:1) to give **8a** in 80% yield (due to partial decomposition on column).

$C_{12}H_{15}N_3O$ (217.3): calc. C 66.34, H 6.96, N 19.34; found C 66.43, H 7.12, N 19.45.

^{1}H NMR: δ = 8.05 (d, 1 H, J = 8.2 Hz), 7.60 (d, 1 H, J = 8.3 Hz), 7.48–7.42 (m, 1 H), 7.38–7.29 (m, 1 H), 6.65 (d, 1 H, J = 12.7 Hz), 5.51–5.43 (m, 1 H), 5.19 (dd, 1 H, J = 12.7, 8.1 Hz), 3.79–3.69 (m, 2 H), 1.86 (d, 3 H, J = 7.0 Hz), 1.26 (t, 3 H, J = 7.0 Hz).

^{13}C NMR: δ = 149.2, 146.4, 131.8, 126.7, 123.6, 119.9, 110.1, 103.3, 65.0, 55.1, 21.4, 14.5.

3-(Benzotriazol-1-yl)-1-ethoxy-3-ethylpent-1-ene (10a):
To a solution of **6** (10 mmol) in THF (40 mL) was added BuLi (2 M, 5.25 mL, 10.5 mmol) at − 78 °C under argon. After 45 min EtI (1.56 g, 10 mmol) was added. The mixture was stirred for 4 h at − 78 °C and allowed to warm to r.t. overnight. The mixture was cooled to − 78 °C, followed by the addition of BuLi (2 M, 5.25 mL, 10.5 mmol). After 2 h, EtI (1.56 g, 10 mmol) was added and the mixture was allowed to gradually warm to r.t. overnight. The same workup as for **8a** gave reasonably pure **10a** as an oil; yield: 2.43 g (94%). Column chromatographic separation for an analytically pure sample gave **10a** in 71% yield due to partial decomposition on column.

$C_{15}H_{21}N_3O$ (259.4): calc. C 69.47, H 8.16, N 16.20; found C 69.81, H 8.42, N 15.93.

^{1}H NMR: δ = 8.04 (dd, 1 H, J = 7.6, 1.3 Hz), 7.72 (dd, 1 H, J = 7.9, 1.3 Hz), 7.40–7.28 (m, 2 H), 6.45 (d, 1 H, J = 13.2 Hz), 5.14 (d, 1 H, J = 13.2 Hz), 3.78 (q, 2 H, J = 7.0 Hz), 2.43–2.25 (m, 4 H), 1.30 (t, 3 H, J = 7.0 Hz), 0.77 (t, 6 H, J = 7.3 Hz).

^{13}C NMR: δ = 148.5, 146.8, 132.6, 126.1, 123.3, 119.9, 112.8, 106.8, 68.3, 65.2, 29.9, 14.7, 7.8.

1-(Benzotriazol-1-yl)-1-ethoxy-3-ethylpent-2-ene (12a):
To a solution of crude **10a** prepared in situ from **6** (20 mmol) in hexanes was added silica gel (8 g) (dried at 180 °C for 8 h prior to use). The mixture was refluxed for 8 h. After filtration, the silica gel was washed with CH_2Cl_2 (3 × 10 mL) and the filtrates were combined. Evaporation of the solvent gave **12a** as an oil; yield: 2.48 g (92%).

HRMS: m/z calculated for $C_{15}H_{22}N_3O$ 260.1763; found 260.1743.

^{1}H NMR: δ = 8.08 (d, 1 H, J = 8.3 Hz), 7.81 (d, 1 H, J = 8.3 Hz), 7.51–7.36 (m, 2 H), 6.82 (d, 1 H, J = 7.2 Hz), 5.80 (d, 1 H, J = 7.2 Hz), 3.63–3.57 (m, 1 H), 3.30–3.25 (m, 1 H), 2.23–2.05 (m, 4 H), 1.16 (t, 3 H, J = 7.0 Hz), 1.02 (t, 3 H, J = 7.4 Hz), 0.88 (t, 3 H, J = 7.7 Hz).

^{13}C NMR: δ = 151.4, 146.7, 131.0, 127.2, 124.0, 119.9, 118.1, 111.4, 86.8, 64.0, 28.6, 24.2, 14.6, 12.6, 11.9.

α,β-Unsaturated Aldehydes 9a,b; General Procedure:
To a solution of crude **8** [prepared in situ from **6** (1.01 g, 5 mmol) and an electrophile (5 mmol) by the same procedure as for **8a**] in THF (40 mL) was added $ZnBr_2$ (2.25 g, 10 mmol) and H_2O (5 mL). The mixture was refluxed for 0.5 h. Et_2O (100 mL) and H_2O (100 mL) were added. The organic layer was washed with H_2O (2 × 50 mL) and dried ($MgSO_4$). In the case of **9a**, after the solvent was removed, the residue was treated with a solution of 2,4-dinitrophenylhydrazine (0.99 g, 5 mmol) and conc. H_2SO_4 (10 mL) in THF (10 mL). The precipitate was filtered and purified by recrystallization to give pure **9a**; yield: 0.98 g (82%). In the case of **9b**, after the solvent was removed, the residue was subjected to column chromatography (hexanes) to give pure **9b**; yield: 0.33 g (40%).

2,4-Dinitrophenylhydrazine Derivative of 5-Phenylpent-2-enal **(9a)**: 2-Phenylethyl bromide was used as the electrophile to afford a yellow powder, mp 164–166 °C.

^{1}H NMR (DMSO-d_6): δ = 11.33 (s, 1 H), 9.00 (d, 1 H, J = 2.6 Hz), 8.29 (dd, 1 H, J = 9.7, 2.6 Hz), 8.14 (dd, 1 H, J = 5.7, 2.5 Hz), 7.94 (d, 1 H, J = 9.7 Hz), 7.33–7.18 (m, 5 H), 6.33–6.30 (m, 2 H), 2.83 (t, 2 H, J = 7.5 Hz), 2.64–2.57 (m, 2 H).

^{13}C NMR (DMSO-d_6): δ = 151.0, 144.3, 143.5, 140.5, 136.8, 129.1, 128.6, 127.9, 127.1, 125.6, 122.7, 118.0, 116.3, 34.2, 34.1.

3-Phenylthioprop-2-enal **(9b)**: Phenyl disulfide was used as the electrophile to afford an oil.

^{1}H NMR: δ = 9.43 (d, 1 H, J = 7.7 Hz), 7.68 (d, 1 H, J = 15.0 Hz), 7.53–7.43 (m, 5 H), 5.98 (dd, 1 H, J = 15.0, 7.7 Hz).

^{13}C NMR: δ = 189.7, 156.7, 133.3, 129.9, 129.7, 129.5, 127.0.

α,β-Unsaturated Aldehydes 11a–c; General Procedure:
To a solution of crude **10** [prepared in situ from **6** (1.01 g, 5 mmol) and two electrophiles (5 mmol respectively) by the same procedure as for **10a**] in THF (40 mL) was added $ZnBr_2$ (2.25 g, 10 mmol) and H_2O (5 mL). The mixture was refluxed for 0.5 h. Et_2O (100 mL) and H_2O (100 mL) were added. The organic layer was washed with H_2O (2 × 50 mL) and dried ($MgSO_4$). After the solvent was removed, the residue was subjected to column chromatography (hexanes) to give pure **11**.

3-Butylhept-2-enal **(11a)**: oil; yield: 0.65 g (78%).

^{1}H NMR: δ = 10.00 (d, 1 H, J = 8.2 Hz), 5.88 (d, 1 H, J = 8.2 Hz), 2.58 (t, 2 H, J = 7.4 Hz), 2.24 (t, 2 H, J = 7.5 Hz), 1.57–1.30 (m, 8 H), 0.96 (t, 3 H, J = 7.3 Hz), 0.94 (t, 3 H, J = 7.2 Hz).

^{13}C NMR: δ = 191.0, 168.9, 127.1, 37.7, 31.7, 31.1, 29.5, 22.7, 22.4, 13.8, 13.7.

3-Ethyloct-2-enal **(11b)**: a mixture of *cis* and *trans*, oil; yield: 0.58 g (76%).

^{1}H NMR: δ = 10.01 (d, 1 H, J = 8.2 Hz), 5.89–5.82 (m, 1 H), 2.64–2.55 (m, 2 H), 2.29–2.22 (m, 2 H), 1.57–1.39 (m, 2 H), 1.37–1.30 (m, 5 H), 1.21–1.09 (m, 2 H), 0.98–0.89 (m, 3 H).

^{13}C NMR: δ = 191.2 (*cis*), 191.0 (*trans*), 170.3 (*cis*), 170.1 (*trans*), 126.4 (*trans*), 126.1 (*cis*), 37.6 (*cis*), 31.7 (*trans*), 31.4 (*cis* and *trans*), 30.8 (*cis*), 29.3 (*trans*), 27.0 (*cis*), 24.4 (*trans*), 22.4 (*cis*), 22.3 (*trans*), 14.3 (*cis*), 13.9 (*cis* and *trans*), 11.7 (*trans*).

3-Ethylhept-2-enal **(11c)**: oil; yield: 0.50 g (72%).

^{1}H NMR: δ = 10.04–10.00 (m, 1 H), 5.87 (d, 1 H, J = 8.5 Hz), 2.62–2.56 (m, 2 H), 2.30–2.22 (m, 2 H), 1.57–1.33 (m, 5 H), 1.22–1.10 (m, 2 H), 0.98–0.92 (m, 3 H).

^{13}C NMR: δ = 191.1 (*cis*), 191.0 (*trans*), 169.4 (*cis*), 168.8 (*trans*), 127.1 (*trans*), 126.1 (*cis*), 37.7 (*cis*), 37.5 (*trans*), 31.7 (*trans*), 31.2 (*cis*), 31.0 (*trans*), 30.5 (*cis*), 29.5 (*trans*), 29.4 (*cis*), 22.8 (*trans*), 22.3 (*cis*), 13.7 (*trans*), 11.7 (*cis*).

α,β-Unsaturated Ketones 13a,b; General Procedure:
To a solution of crude **12** [prepared in situ from **6** (1.01 g, 5 mmol) and two electrophiles (5 mmol respectively) by the same procedure as for **12a**] in THF (40 mL) was added BuLi (2 M, 2.75 mL, 5.5 mmol) at − 100 °C under argon. After 8 min a third electrophile (5.5 mmol) was added. The mixture was allowed to warm gradually to r.t. overnight. H_2O (60 mL) and conc. HCl (10 mL) were added and the mixture was stirred at r.t. for 15 h. Et_2O (150 mL) and H_2O (80 mL) were added. The organic layer was washed with sat. Na_2CO_3 (2 × 80 mL) and H_2O (80 mL). After drying ($MgSO_4$), the solvent was removed and the residue was subjected to chromatography (hexanes) to give pure **13**.

3-Butylhept-2-enacyl(dimethyl)octylsilane **(13a)**: Butyl iodide was used as the first and second electrophile and dimethyl(octyl)silyl iodide as the third electrophile to afford an oil; yield: 1.12 g (66%).

^{1}H NMR: δ = 6.42 (s, 1 H), 2.36 (t, 2 H, J = 7.9 Hz), 2.03 (t, 2 H, J = 7.5 Hz), 1.42–1.18 (m, 20 H), 0.88–0.78 (m, 9 H), 0.62 (t, 2 H, J = 7.5 Hz), 0.10 (s, 3 H), 0.09 (s, 3 H).

^{13}C NMR: δ = 237.7, 158.0, 126.6, 38.2, 33.4, 32.7, 31.9, 31.2, 30.0, 29.2, 23.7, 23.1, 22.7, 22.5, 14.1, 14.0, 13.9, 13.8, −4.8.

8-Butyldodec-7-en-6-one **(13b)**: Butyl iodide was used as the first and second electrophile and pentyl iodide as the third electrophile to afford an oil; yield: 0.59 g (50%).

^{1}H NMR: δ = 6.03 (s, 1 H), 2.57 (t, 2 H, J = 7.2 Hz), 2.42 (t, 2 H, J = 7.7 Hz), 2.14 (t, 2 H, J = 7.2 Hz), 1.70–1.28 (m, 14 H), 0.97–0.89 (m, 9 H).

^{13}C NMR: δ = 201.1, 163.2, 122.7, 44.5, 38.4, 32.3, 31.5, 30.8, 30.0, 24.0, 23.1, 22.5, 13.9.

Pyrroles 17a–c; General Procedure:
To a solution of **6** (1.01 g, 5 mmol) in THF (40 mL) was added BuLi (2 M, 2.75 mL, 5.5 mL) at −78 °C under argon. After 0.5 h, a solution of an appropriate imine (5 mmol) in THF (10 mL) was added. The mixture was allowed to warm gradually to r.t. overnight. $ZnBr_2$ (2.25 g, 10 mmol) was added and the mixture was refluxed for 8 h. H_2O (150 mL) was added and the mixture was extracted with Et_2O (2 × 100 mL). The combined organic layer was dried ($MgSO_4$) and the solvent was removed. The residue was subjected to chromatography (hexanes: EtOAc = 20:1) to give pure **17**.

1,2-Diphenylphenylpyrrole **(17a)**: solid; yield: 0.60 g (55%), mp 80–82 °C.

^{1}H NMR: δ = 7.36–7.12 (m, 10 H), 6.96–6.94 (m, 1 H), 6.46–6.44 (m, 1 H), 6.39–6.36 (m, 1 H).

^{13}C NMR: δ = 140.5, 133.8, 133.0, 129.0, 128.3, 128.0, 126.6, 126.2, 125.7, 124.4, 110.7, 109.2.

2-(4-Methoxyphenyl)-1-phenylpyrrole **(17b)**: oil; yield: 0.71 g (57%).

^{1}H NMR: δ = 7.28–7.11 (m, 5 H), 7.05–7.02 (m, 2 H), 6.89–6.87 (m, 1 H), 6.73–6.70 (m, 2 H), 6.36–6.31 (m, 2 H), 3.69 (s, 3 H).

^{13}C NMR: δ = 158.1, 140.5, 133.5, 129.5, 128.9, 126.4, 125.6, 123.6, 113.5, 109.8, 109.3, 55.0.

1-(4-Chlorophenyl)-2-phenylpyrrole **(17c)**: solid; yield: 0.79 g (63%), mp 74–76 °C.

^{1}H NMR: δ = 7.28–7.07 (m, 9 H), 6.89 (dd, 1 H, J = 3.0, 2.0 Hz), 6.43 (dd, 1 H, J = 3.0, 2.0 Hz), 6.36 (t, 1 H, J = 3.0 Hz).

^{13}C NMR: δ = 139.0, 133.8, 132.6, 132.2, 129.1, 128.3, 128.2, 126.8, 126.5, 124.2, 111.0, 109.6.

Furans 19a–c; General Procedure:
To a solution of crude **8** [prepared in situ from **6** (1.01 g, 5 mmol) and an alkyl iodide (5 mmol) by the same procedure as for **8a**] in THF (40 mL) was added BuLi (2 M, 2.75 mL, 5.5 mmol) at −78 °C under argon. After 2 h, an aldehyde (5.5 mmol) was added and the mixture was allowed to warm gradually to r.t. overnight. $ZnBr_2$ (2.25 g, 10 mmol) was added and the mixture was refluxed for 8 h. The same workup procedure as for pyrroles **17** gave pure **19**.

3-Butyl-2-(4-methylphenyl)furan **(19a)**: oil; yield: 0.49 g (46%).

^{1}H NMR: δ = 7.49 (d, 2 H, J = 7.9 Hz), 7.34 (d, 1 H, J = 1.5 Hz), 7.19 (d, 2 H, J = 7.9 Hz), 6.34 (d, 1 H, J = 1.5 Hz), 2.63 (t, 2 H, J = 7.7 Hz), 2.35 (s, 3 H), 1.66–1.55 (m, 2 H), 1.43–1.36 (m, 2 H), 0.92 (t, 3 H, J = 7.1 Hz).

^{13}C NMR: δ = 148.6, 140.5, 136.5, 129.2 (2C), 125.6, 120.9, 113.3, 32.2, 25.5, 22.6, 21.2, 13.9.

3-Butyl-2-propylfuran **(19b)**: oil; yield: 0.41 g (49%).

^{1}H NMR: δ = 7.21 (d, 1 H, J = 1.8 Hz), 6.18 (d, 1 H, J = 1.8 Hz), 2.53 (t, 2 H, J = 7.4 Hz), 2.32 (t, 2 H, J = 7.5 Hz), 1.66–1.59 (m, 2 H), 1.52–1.44 (m, 2 H), 1.39–1.30 (m, 2 H), 0.95–0.89 (m, 6 H).

^{13}C NMR: δ = 151.0, 139.7, 119.0, 111.3, 32.8, 27.9, 24.4, 22.4, 22.0, 13.9, 13.7.

3-Ethyl-2-phenylfuran **(19c)**: oil; yield: 0.44 g (52%).

^{1}H NMR: δ = 7.60 (d, 2 H, J = 8.3 Hz), 7.42–7.37 (m, 3 H), 7.27–7.25 (m, 1 H), 6.39 (d, 1 H, J = 1.8 Hz), 2.69 (q, 2 H, J = 7.4 Hz).

^{13}C NMR: δ = 148.1, 141.0, 131.8, 128.5, 126.8, 125.6, 123.0, 113.0, 19.1, 14.5, 1.25 (t, 3 H, J = 7.4 Hz).

Allyl Ethers 20a–c; General Procedure:
To a solution of crude **8** [prepared in situ from **6** (1.01 g, 5 mmol) and an alkyl halide (5 mmol) by the same procedure as for **8a**] in THF (40 mL) was added an appropriate Grignard reagent (20 mmol) in toluene (30 mL). The mixture was refluxed for 8 h and H_2O (100 mL) was added. The organic layer was dried ($MgSO_4$) and the solvent evaporated. The residue was subjected to column chromatography (hexanes: EtOAc = 10:1) to give pure **20**.

Ethyl (1-Methyl-5-phenyl)pent-2-enyl Ether **(20a)**: 2-Phenylethyl bromide was used as the alkyl halide and MeMgI as the Grignard reagent to afford an oil; yield: 0.69 g (68%).

^{1}H NMR: δ = 7.30–7.26 (m, 2 H), 7.23–7.16 (m, 3 H), 5.61 (dt, 1 H, J = 15.4, 6.6 Hz), 5.40–5.31 (m, 1 H), 3.79–3.74 (m, 1 H), 3.47–3.33 (m, 1 H), 3.31–3.23 (m, 1 H), 2.71 (m, 2 H), 2.40–2.32 (m, 2 H), 1.22–1.14 (m, 6 H).

^{13}C NMR: δ = 141.7, 133.1, 131.2, 128.4, 128.2, 125.8, 76.1, 63.1, 35.7, 33.9, 21.7, 15.4.

Ethyl (1-Phenyl)but-2-enyl Ether **(20b)**: Methyl iodide was used as the alkyl halide and PhMgBr as the Grignard reagent to afford an oil; yield: 0.62 g (71%).

^{1}H NMR: δ = 7.36–7.33 (m, 4 H), 7.29–7.26 (m, 1 H), 5.68–5.63 (m, 2 H), 4.69 (d, 1 H, J = 6.0 Hz), 3.54–3.51 (m, 1 H), 3.48–3.38 (m, 1 H), 1.71 (d, 3 H, J = 5.0 Hz), 1.23 (t, 3 H, J = 7.0 Hz).

^{13}C NMR: δ = 142.1, 132.5, 128.3, 127.7, 127.3, 126.6, 82.6, 63.6, 17.7, 15.3.

Ethyl (1-Ethyl-4-phenyl)but-2-enyl Ether **(20c)**: Benzyl bromide was used as the alkyl halide and EtMgI as the Grignard reagent to afford an oil; yield: 0.61 g (60%).

^{1} NMR: δ = 7.32–7.17 (m, 5 H), 5.75 (m, 1 H), 5.44–5.36 (m, 1 H), 3.60–3.52 (m, 2 H), 3.40 (d, 2 H, J = 7.1 Hz), 3.36–3.30 (m, 1 H), 1.67–1.47 (m, 2 H), 1.19 (t, 3 H, J = 7.0 Hz), 0.89 (t, 3 H, J = 7.4 Hz).

^{13}C NMR: δ = 140.3, 132.6, 131.8, 128.5, 128.3, 126.0, 81.9, 63.5, 38.7, 28.5, 15.3, 9.9.

Allyl Ethers 21a,b; General Procedure:
To a solution of crude **10** [prepared in situ from **6** (1.01 g, 5 mmol) and two electrophiles (5 mmol, respectively) by the same procedure as for **10a**] in THF (40 mL) was added a Grignard reagent (20 mmol) in toluene (30 mL). After refluxing for 5 h, H_2O (100 mL) and Et_2O (100 mL) were added. The organic layer was dried ($MgSO_4$) and the solvent removed. The residue was purified by vacuum distillation to give pure **21**.

Ethyl (3-Butyl-1-phenyl)hept-2-enyl Ether **(21a)**: Butyl iodide was used as electrophile twice and PhMgBr as the Grignard reagent to afford an oil; yield: 1.04 g (76%).

^{1}H NMR: δ = 7.37–7.21 (m, 5 H), 5.32 (d, 1 H, J = 9.1 Hz), 5.03 (d, 1 H, J = 9.1 Hz), 3.53–3.36 (m, 2 H), 2.19–2.14 (m, 2 H), 2.05–1.99 (m, 2 H), 1.45–1.19 (m, 11 H), 0.95–0.85 (m, 6 H).

^{13}C NMR: δ = 143.5, 143.0, 128.3, 127.1, 126.6, 125.9, 77.6, 63.3, 36.5, 30.8, 30.6, 30.2, 23.0, 22.6, 15.4, 14.0.

Ethyl (3-Ethyl-1-phenyl)pent-2-enyl Ether **(21b)**: Ethyl iodide was used as the electrophile twice and PhMgBr as the Grignard reagent to afford an oil; yield: 0.85 g (78%).

^{1}H NMR: δ = 7.40–7.24 (m, 5 H), 5.32 (d, 2 H, J = 8.9 Hz), 5.07 (d, 1 H, J = 8.9 Hz), 3.55–3.38 (m, 2 H), 2.26–2.12 (m, 2 H), 2.10–2.05 (m, 2 H), 1.24 (t, 3 H, J = 7.0 Hz), 1.07–1.00 (m, 6 H).

^{13}C NMR: δ = 146.1, 143.0, 128.3, 127.1, 126.6, 124.3, 77.7, 63.4, 29.0, 24.0, 15.4, 13.3, 12.4.

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